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Hydrogen assisted catalytic biomass pyrolysis for green fuels

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Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies [1]. To utilize this oil as liquid transportation fuel the oxygen content must be reduced from 15-30 wt.% down to <1 wt.%, which increases heating value and stability and decreases acidity [1]. Upgrading bio-oil by hydrodeoxygenation (HDO) is challenged by severe coking upon heating the oil. Alternatively, performing fast pyrolysis in high-pressure hydrogen atmosphere in a fluid bed reactor with a HDO catalyst as bed medium, could immediately stabilize reactive pyrolysis vapors [2]. A schematic diagram for such a process is shown in Figure 1. A simplified bench scale setup has been constructed at DTU Chemical Engineering for proof-of-concept for the continuous conversion of solid biomass to low oxygen, fuel-grade bio-oil.

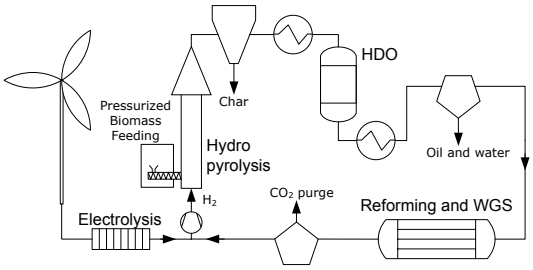

Figure 1: Simplified process diagram including fluid bed catalytic hydropyrolysis, char separation, temperature adjustment, vapor phase HDO reactor, cooling, condensation and liquid separationSteam reforming and water gas shift (WGS) of non-condensable gasses to produce H_2 and wind-powered electrolysis of water to H_2 is envisioned.

Experiments were performed with a sulfided $CoMo/MgAl_2O_4$ catalyst in the fluid bed reactor and a sulfided $NiMo/Al_2O_3$ catalyst in the HDO reactor. Hydropyrolysis of beech wood was performed at 25 bar with gas composition 470 ppm H_2S, 6 % N_2 balance H_2. The effect of varying the temperature (365-511 °C) and hydrogen pressure (15-35 barg) on the product yield and organic composition was studied. The mass balance closed between 90 and 101 wt. % dry ash free basis (daf). The combined condensed organics and C_{4+} gasses yield varied between 17 and 22 wt. % daf (Figure 2), which corresponds to an energy recovery between 40 and 53 % in the organic product. The yield of non-condensable gasses varied between 24 and 32 wt. % daf and the char yield varied between 9.6 and 18 wt. %. GC simulated distillation showed that the condensed organics consisted of 20-40 vol. % naphtha and 60-80 vol. % diesel. The organics contain 42 to 75 wt. % aromatics, based on GC×GC-FID chromatographic peak area, and the remainder was primarily naphthenes. The condensed organics were essentially oxygen free (<0.001 wt. %) when both reactors were used. Bypassing the HDO reactor increased the oxygen content in the condensed liquid to 1.8 wt. %. In the ongoing work the effect of the choice of catalyst in the fluid bed is investigated and a combined organic and C_{4+} gas yield of 25 wt.% daf has been obtained. The results show that catalytic hydropyrolysis may be a viable way to process solid biomass into liquid and gaseous hydrocarbon fuels.

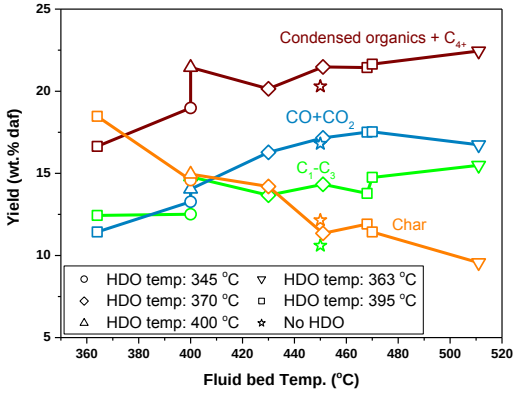

Figure 2: Effect of the fluid bed temperature.

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[2] T.L. Marker, L.G. Felix, M.B. Linck, M.J. Roberts, Environ. Prog. Sustain. Energy 31 (2012) 191.